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(54) Title: PIGMENT MATERIALS AND THEIR PREPARATION AND USE
 (54) Titre: MATIERES PIGMENTAIRES; PREPARATION ET UTILISATION ASSOCIEES

(57) Abstract

A method of preparing and using a composite pigment material which incorporates a fine particulate material, which method comprises the steps of: (a) treating an aqueous medium containing dispersed particles of a fine particulate material by chemically reacting therein a first reactant and a second reactant to precipitate therein crystals of a white insoluble pigment compound thereby forming in the aqueous medium a composite pigment material comprising a composite matrix of precipitated crystals of the white pigment compound and particles of the fine particulate material dispersed and bonded within the matrix wherein the first and second reactants are such that they react together without producing a substantial amount of non-crystalline by-product; and (b) adding the composite material to a composition for forming or coating a fibrous sheet material. The method may thereafter include (c) forming or coating a fibrous sheet material using the composition incorporating the composite material. The said aqueous medium employed in step (a) may comprise an aqueous suspension or slurry.

(57) Abrégé

L'invention concerne un procédé de préparation et d'utilisation d'une matière pigmentaire composite comprenant une matière à fines particules. Le procédé de préparation comprend les étapes suivantes: (a) traiter un milieu aqueux contenant des particules dispersées d'une matière à fines particules par réaction chimique avec un premier réactif et un second réactif de manière à précipiter des cristaux d'un composé pigmentaire insoluble blanc afin de former, dans ce milieu aqueux, une matière pigmentaire composite comprenant une matrice composite formée, d'une part, de cristaux précipités du composé pigmentaire blanc et, d'autre part, de particules de la matière à fines particules, laquelle matrice est dispersée et liée à l'intérieur même de la matrice; le premier réactif et le second réactif étant tels qu'ils réagissent ensemble sans produire une quantité significative de sous-produit non cristallin; et (b) ajouter la matière composite à une composition de manière à former ou à recouvrir un matériau en feuille fibreux. Le procédé de fabrication peut également comprendre une étape consistant à (c) former ou recouvrir un matériau en feuille fibreux à l'aide d'une composition contenant la matière composite. Le milieu aqueux utilisé lors de l'étape (a) peut comprendre une suspension aqueuse ou une pâte.

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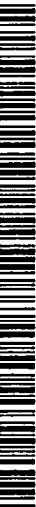
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(54) Title: PIGMENT MATERIALS AND THEIR PREPARATION AND USE

(57) Abstract: A method of preparing and using a composite pigment material which incorporates a fine particulate material, which method comprises the steps of: (a) treating an aqueous medium containing dispersed particles of a fine particulate material by chemically reacting therein a first reactant and a second reactant to precipitate therein crystals of a white insoluble pigment compound thereby forming in the aqueous medium a composite pigment material comprising a composite matrix of precipitated crystals of the white pigment compound and particles of the fine particulate material dispersed and bonded within the matrix wherein the first and second reactants are such that they react together without producing a substantial amount of non-crystalline by-product; and (b) adding the composite material to a composition for forming or coating a fibrous sheet material. The method may thereafter include (c) forming or coating a fibrous sheet material using the composition incorporating the composite material. The said aqueous medium employed in step (a) may comprise an aqueous suspension or slurry.

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TITLE OF THE INVENTION

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Pigment materials and their preparation and useBACKGROUND OF THE INVENTION

5 The present invention relates to pigment
15 materials and their preparation and use. In
 particular, it relates to new pigment material
 comprising a composite containing a fine particulate
 material such as titanium dioxide and to the
20 10 preparation of such material and its use in
 operations to make or coat paper and the like sheet
 materials.

25 Titanium dioxide, herein "TiO₂", is an example of
 a fine particulate material which, unlike materials
15 15 which are employed as bulk fillers, is employed for a
 specific function in paper making and paper coating
 operations. It offers excellent pigment opacity and
 brightness (which together result in excellent light
 scattering) and is therefore used to extend these
20 20 properties in a paper making or coating composition.
 TiO₂ is a very expensive material and is consequently
 used only sparingly in paper making or coating
 compositions, eg usually forming less than 5% by
 weight of the solids present in the composition.
35 35 25 Because of its cost, TiO₂ needs to be employed as
 efficiently as possible.

40 40 45 The optimum particle size for TiO₂ pigment
 particles to give the best light scattering
 properties has been determined in the prior art to be
30 30 35 about 0.2μm to 0.3μm. TiO₂ pigment material is
 normally supplied commercially in a form wherein the

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10 particles have this optimum size. The TiO₂ product may be supplied dry, in which case it requires dispersion in liquid media to wet and to deagglomerate or disperse the particles.

15 5 Alternatively, TiO₂ may be supplied commercially in a pre-dispersed slurry form which may incorporate a relatively large amount of anionic stabiliser.

Since the TiO₂ particles employed in paper making are very fine and are usually dispersed with

20 10 relatively high levels of dispersant to make slurries containing the material pumpable and to maximise the spacing between particles to give optimal light scatter, it is difficult to retain such particles when they are employed in a furnish or like
25 15 composition in a paper or like sheet forming operation.

In order to improve TiO₂ retention in such operations, in order to minimise TiO₂ losses, various chemical retention aids are employed in the prior

30 20 art. In general, such aids are expensive chemicals, eg water soluble polymers, and the extent of use of such chemicals employed for the conventional retention of TiO₂ is considered to be very costly.
35 Where the TiO₂ is supplied with anionic stabiliser
40 25 large amounts of cationic chemicals (which may also serve as or be delivered together with retention aids) may be required to reduce the anionic loading.

TiO₂ particles (when used in a pigment-containing composition) have a tendency to agglomerate especially at higher loading levels, this effect being known was 'crowding'. Use of retention aid

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10 chemicals can increase crowding which has been demonstrated in the prior art to have an adverse effect on the light scattering efficiency of the particles. This can result in degradation of the
5 expected optical properties of commercially available
15 TiO_2 material when used as a particulate pigment material in paper.

Furthermore, such added chemicals when used in substantial quantities to improve TiO_2 retention, have
20 an adverse effect on the formation of the paper or other sheet being produced and can result in sheets of less than ideal quality in which the constituents of the sheet are not uniformly distributed.

25 Attempts have been reported in the prior art to
15 counteract the effects of crowding of fine particulate material, especially TiO_2 , by forming
30 composites of the particles of the material to space the particles from one another. These attempts have been aimed primarily at improving the optical
20 properties of the compositions to which the composite material is added.

35 One method of the prior art which involves titanium dioxide TiO_2 , is described in US Patent No 2,170,800 wherein a mixture of TiO_2 and CaSO_4 is
40 reacted with a solution of Na_2CO_3 to convert CaSO_4 to CaCO_3 and precipitate a composite pigment comprising TiO_2 and CaCO_3 . Another method for producing a TiO_2 -
45 CaCO_3 composite pigment is described in US Patent No 3,528,838 in which a solution of Na_2CO_3 and a solution
30 of CaCl_2 are employed. Pigmentary TiO_2 is dispersed in one of these solutions and the two solutions are

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mixed to precipitate a TiO_2 - $CaCO_3$ composite pigment.
Still another coalesced composite pigment is
10 described in US Patent No 3,832,206 wherein
 $CaCO_3$ pigmentary TiO_2 is dispersed in a solution of Na_2CO_3 .
5 A slurry of $Ca(OH)_2$ is added to the Na_2CO_3 - TiO_2 mixture
15 in order to react with the Na_2CO_3 and precipitate
 $CaCO_3$. The $CaCO_3$ formed in the presence of the TiO_2
pigment particles results in a coalesced composite
pigment of TiO_2 - $CaCO_3$. In each of these three prior
20 art processes, the composite pigment product must,
before it can be used in paper making, be separated
from the aqueous phase in which it is formed and
washed free of the by-product resulting from the
chemical reaction involved in producing $CaCO_3$. This
25 by-product is Na_2SO_4 in case of US Patent No
2,170,800, $NaCl$ in case of US Patent No 3,528,838 and
 $NaOH$ in case of US Patent No 3,832,206. Removing the
30 by-product in each case is time consuming and costly.
In US Patent No 4,028,173, Olson describes the
use of a physical mixture of $CaCO_3$ and TiO_2 in the
manufacture of papers.
35 Another avenue of producing carbonate
agglomerates consists of utilizing organic chemicals
or silicates to bind the aggregates. The following
40 25 prior published patents disclose the use of such
binders. In US Patent No 4,072,537, to F L Kurrel, a
composite silicate pigment is prepared by a
precipitation reaction employing an aqueous
45 suspension of clay particles wherein spherical
30 hydrous metal silicates particles are precipitated on
the planar surface of the clay. In US Patent No

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4,816,074 by Ravthatha et al, a process is described
in which a structured aggregated kaolin pigment is
10 prepared by mixing substantially dry kaolin in
particulate form with an aqueous alkali metal
silicate to deposit on the surface of the kaolin
15 particles a substantially molecular level of said
silicate without formation of silica gel, drying the
treated kaolin without calcination and exposing it to
an acidic gas. The product is useful as a pigment in
20 the coating or filling of paper. In a further aspect
of the invention, it is preferable to intermix with
the kaolin feed, small quantities of an aggregation
agent. Such agent is selected from one or more
25 members of the group consisting of the alkaline earth
metal carbonate, chlorides or hydroxides or lithium
carbonate.

Polyacrylate alkali metal salts are known as
30 dispersants for clay, eg kaolin. Sodium polyacrylate
is a common dispersant, frequently used in the
refining/working up the crude material. However, US
35 Patent No 5,082,887 describes a pigment composition
for the coating and filling of paper comprising a
dispersion of an aqueous phase, a pigment or mixture
of pigments such as kaolin, titanium dioxide and
40 calcium carbonate, gypsum, mica and a dispersing
agent comprised of carboxyl-containing polymers, eg
an acrylic polymer, at least 60% of which is
converted to the salt form with a polyvalent cation,
45 calcium, and if desired the balance may be converted
30 with a monovalent cation such as sodium, ammonium and
quaternary amine cations. Gaseous carbon dioxide is

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10 added to the slurry, and reacts, with the remaining calcium ion to precipitate calcium carbonate onto the polymeric carboxyl calcium salt. The resultant composite aggregates are recovered and dried, as
5 product.

15 The problem of maintaining a reasonable retention of TiO₂ particles in a paper making operation, whilst at the same time avoiding agglomeration or crowding and an adverse effect on
20 formation caused by the addition of chemicals to facilitate retention, has not satisfactorily been solved in the prior art. One purpose of the present invention is to provide a novel solution to this
25 problem.

30 15 Similar problems arise with the retention of other fine particulate materials, and it is another purpose of the present invention to provide a novel solution to the retention of such materials.

35 It is a further purpose of this invention to
20 produce a novel pigment material which is useful in paper coating.

40 35 In the light of the foregoing, it may also be regarded as an object of the present invention, to provide a structural composite pigment, such as a
45 25 composite titanium dioxide/calcium carbonate, kaolin/calcium carbonate, alumina/calcium carbonate, silica/calcium carbonate, mica/calcium carbonate, gypsum/calcium carbonate which possesses improved light scattering characteristics, and hence is useful
30 30 as an opacifier and light scattering filler for paper and paper products, and which may similarly be used

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in other paper manufacturing applications, including
10 in the coating of the same.

10 It is yet a further object of the present
invention, to provide a method for producing
5 structured composite mineral pigments as
15 aforementioned, which consists of a minimal number of
simply conducted steps, which utilize relatively
simple and inexpensive apparatus.

20 It is a further object of the present invention,
10 to provide a method for producing a pigment with good
retention properties in the paper web of the
25 expensive component of the aggregate pigment.
Furthermore, the method provides a pigment without
subjecting to any purification or calcination step.

30 15 It is yet a further object of the present
invention, to provide a pigment with a cationic zeta
potential which decreases charge demand as compared
to anionic or anionic dispersed pigments of the prior
art.

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35 SUMMARY OF THE INVENTION
The above purposes and objects and others which
will become apparent from this specification are met
by the present invention.

40 25 The present invention is concerned with a method
for the preparation and use of structured composite
pigments, which can, amongst other things, improve
the retention of fine particulate material such as
45 TiO₂ in paper making compositions without seriously
30 affecting optical or other properties, in some cases
beneficially improving such properties also. The

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resulting composite pigments can also be used
beneficially in paper coating.

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According to the present invention in a first aspect there is provided a method of preparing and
5 using a composite pigment material which incorporates a fine particulate material, which comprises (a) treating an aqueous medium containing dispersed particles of a fine particulate material by chemically reacting therein a first reactant and a
10 second reactant to precipitate therein crystals of a white insoluble pigment compound thereby forming in the aqueous medium a composite matrix of precipitated crystals of the white pigment compound and particles of the fine particulate material dispersed and bonded
15 within the matrix wherein the first and second reactants are such that they react together without producing a substantial amount of non-crystalline by-product; and (b) adding the composite material to a
20 composition for forming or coating a fibrous sheet material. The method may thereafter include (c) forming or coating a fibrous sheet material using the
25 composition incorporating the composite material. The said aqueous medium employed in step (a) may comprise an aqueous suspension or slurry.

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25 The fine particulate material and the first and second reactants employed to produce the precipitation reaction may be obtained from separate stocks and may be added together prior to step (a) to produce the composite pigment material. Either or both of these materials may be in dry or wet (eg slurry) form when they are added together.

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At least part of the fine particulate material
may comprise fresh particles. By 'fresh' particles
of fine particulate material is meant particles which
have not previously been used in a sheet forming or
coating or other operation.

The fibrous sheet material formed or coated in
step (c) may comprise paper, paper board, card,
cardboard, laminated paper and the like herein
collectively called 'paper', wherein the fibrous
sheet material comprises organic, eg cellulosic
fibres, and in many cases also inorganic filler
comprising a particulate pigment material.

By "fine particulate material" is meant a
particulate material wherein the particles have a
size distribution such that at least 90% by weight
have an esd (equivalent spherical diameter as
measured in a known way by sedimentation) of less
than 2 μm . At least 50 per cent by weight may have an
esd less than 1 μm . The mean particle size of the
particles of the fine particulate material may for
example be in the range 0.1 μm to 1.5 μm especially
0.1 μm to 0.7 μm . The fine particulate material will
generally be one which is more expensive than bulk
filler materials (eg conventional kaolin and/or
calcium carbonate) and one which is used in paper for
a specific function (other than bulk filling) and
generally has a poor natural retention in paper
making.

The present invention is especially beneficial
where the fine particulate material comprises TiO₂,
although the particulate material may alternatively,

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or in addition, be selected from calcined kaolin,
fine silica, eg so called fumed silica, sodium
10 silicate, aluminium silicate, sodium aluminium
silicate, talc, calcium sulfate, alumina, mica and so
5 called plastic pigment materials, eg produced from
melamine formaldehyde and mixtures of these
15 materials. It should be noted that calcined material
may contain aggregates of fine particles fused or
sintered together but the fine particles which make
20 up such aggregates may have the required particle
size distribution properties if measured
individually.

The said white insoluble pigment compound which
25 is precipitated in the method according to the first
15 aspect of the present invention may comprise a water
insoluble salt, ie it may be formed from or regarded
as formed from an acid and a base. It may comprise a
30 simple salt formed from a single anion and a single
cation. It may conveniently comprise an alkaline
20 earth metal carbonate, eg calcium carbonate, produced
by reacting carbon dioxide with a suitable hydroxide,
eg calcium hydroxide. Reactants (eg providing acidic
35 and basic species) to produce the white insoluble
pigment compound may be added together or separately
25 to the aqueous medium.

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DESCRIPTION OF THE INVENTION

The composite pigment material according to the
45 present invention comprises a fine particulate
30 material dispersed and bonded within a matrix formed
of crystals of a precipitated white insoluble

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inorganic compound, eg calcium carbonate. The parent application, US Serial No 08/957,280 describes such a composite material but in that case a substantial amount of fibers are also added to the aqueous suspension to be contained within the composite matrix. The production of material according to the present invention need not include deliberate addition of fibers, although in one embodiment of the invention the aqueous medium in which the precipitate crystals are formed may contain fibers already present, eg the aqueous medium may comprise white water from a paper making operation.

By the method of the invention, the particles of the fine particulate material, if suitably dispersed when the precipitation reaction is carried out, unexpectedly and beneficially remain dispersed in the solid composite matrix formed when the bonding crystals of the white pigment compound are precipitated and become cemented to the bonding crystals.

Where the precipitate compound formed is a basic compound, eg calcium carbonate, it can advantageously be effective in neutralizing any anionic charges present in a paper making or coating composition, eg due to the addition of anionic stabilisers, thereby allowing the amount of any added cationic chemicals to be reduced.

Particulate materials to be used as fillers in paper making usually carry a surface charge when dispersed in water. The surface charge is dependent on pH and chemical species at the crystal surface.

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The zeta potential is a convenient known way to
measure the charge at the plane of shear near the
crystal surface. Precipitated calcium carbonate is
one of the few fillers having a positive zeta
potential. It is well known, eg from "Retention of
Fines and Fillers During Papermaking, Precipitated
Calcium Carbonate", Chapter 14 by J M Gess (TAPPI
Press, Atlanta, GA) that the charge on the surface
of the filler particle has a dramatic influence on
first pass retention. Positively charged fillers are
retained better than negatively charged fillers.

By forming a composite material comprising
particles of fine particulate material such as TiO₂,
and/or one of the other materials referred to
earlier, dispersed and bonded within a solid matrix
of crystals of white pigment compound, a new pigment
structure is provided which can show various
unexpected benefits when used in paper making or
paper coating operations as described hereinafter.

According to the present invention in a second
aspect there is provided a composite pigment material
comprising a composite matrix of precipitated
crystals of white pigment compound and particles of
fine particulate material as defined hereinbefore,
dispersed and bonded within the matrix which
composite material is the product of step (a) of the
method according to the first aspect.

Particles of the composite pigment material
according to the second aspect may be employed in a
known manner as a pigment filler ingredient in
papermaking or as a pigment ingredient in paper

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ccating. Such particles may be the sole filler or
10 pigment source or they may optionally be blended with
conventional or known fillers or pigment particles
employed in such applications, eg selected from one
5 or more of kaolin, calcined kaolin, calcium carbonate
(derived from a natural or synthetic source or
15 composited in a known manner with other materials, eg
derived from waste streams), dolomite, talc, mica or
untreated TiO₂ or other fine particulate material (eg
20 as used in the preparation of the composite pigment
material).

The composite pigment material according to the
second aspect of the present invention may form from
25 1% to 100% by weight of the filler or pigment
15 particles employed in such applications, eg in the
making of a furnish employed in paper making or a
coating composition employed in paper coating, or in
30 specialist sheet coating operations, eg decorative
laminate formation, although it may be blended with
20 other, eg conventional filler or pigment, materials
eg wherein it may form up to 50% by weight, in some
cases up to 80% by weight of the blend. The
35 filler(s) or pigment(s) employed in such applications
will depend upon the use of the filler or pigment.
40 Fillers in papermaking may form up to 40 per cent by
weight (on a dry solids weight basis) of the paper
making composition or furnish. The pigment(s)
employed in coating compositions usually forms up to
45 80% by weight in some cases as high as about 95% (on
30 a dry solids basis) by weight of the composition.

The composite pigment material according to the second aspect of the present invention can allow fine particulate materials such as TiO₂ and the other materials referred to earlier to be much more efficiently retained in a paper making operation.

For example, in contrast to the low retention levels obtained in the prior art for untreated TiO₂ (without application of a retention aid) or for TiO₂ treated with only a small amount of retention aid (eg retention levels of about 30% or less, even 20% or less, as illustrated hereinafter), the retention level of TiO₂ for a single pass in a paper sheet making operation by production and use of the composite material according to the second aspect of the present invention can advantageously be much greater as illustrated hereinafter (depending on the composition of the composite pigment material and the amount of the material loaded into the paper composition). This allows a reduction in the quantity and cost of retention aid chemical(s) employed to retain fine particulate material such as TiO₂, although some retention aid chemical(s) may optionally be added, (eg in the usual manner to the dilute pulp furnish stock from which the paper sheets are to be produced).

Beneficially, reducing the amount of retention aid chemicals can also improve the burst strength (also known as burst index) of the sheet produced and the paper sheet formation, ie the overall quality of the paper sheet produced by providing more uniform distribution of the constituents of the sheet.

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In addition, the sheet so formed may
10 beneficially have a stiffness or 'crackle' which is
greater than that for a comparable sheet made from
fine particulate material such as TiO₂ as in the prior
5 art. This allows, for example, paper of the same
stiffness as comparable prior art sheets to be
15 produced lighter in weight and (for sheets of the
same weight as prior art sheets) more cheaply.

Furthermore, because the fine particulate
20 material is better retained in the paper making
process, less fine particulate material is lost and
it is not necessary to compensate for the usual loss
which is expected to occur by addition of excessive
25 quantities of the material, which, as in the case of
15 TiO₂, can be very expensive.

A further benefit obtained by preparation and
use of composite pigment material according to the
30 second aspect of the present invention in a paper
making or coating operation is that the undesirable
20 crowding (normally obtained as in the prior art) of
particles of the fine particulate material caused or
35 exacerbated by use of added chemicals is reduced and
this allows the adverse effect on scattering of light
from the particles caused by such crowding to be
25 reduced. Since the crystals of the precipitated
pigment compound may themselves be fine and highly
scattering their presence contributes beneficially to
the optical properties of the composite pigment
40 material and may allow further reduction of the
amount of fine particulate material, where pigment
45 material such as TiO₂, which may be employed as

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compared with prior art compositions aimed at giving
similar properties.

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Thus, generally the present invention allows
savings in the amount and cost of fine particulate
5 material employed in paper making and paper coating
as well as in the use of associated expensive
15 chemicals as well as providing improvements in
various properties of the sheet product.

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According to the present invention in a third
10 aspect there is provided a paper or like sheet
material incorporating filler or coating pigment
particles which comprise particles of the composite
pigment material according to the second aspect
25 defined earlier.

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15 Surprisingly and beneficially the formation and
use of a composite pigment material in accordance
with the invention allows certain optical properties,
particularly scattering, of a paper sheet made or
coated with a composition containing the composite
20 pigment material according to the second aspect to be
enhanced beyond the results obtained with simple
35 admixtures of the two materials making up the
composite, ie fine particulate material and white
insoluble pigment compound (eg precipitated calcium
25 carbonate). The present invention therefore offers
an inexpensive way of extending the effectiveness of
40 the two materials making up the composite.

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In the method according to the first aspect of
the present invention if additional particulate
30 solids are present, other than consumable reagent(s)
employed to form the precipitate compound, in the

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aqueous medium in which the precipitation reaction is
carried out the amount of such solids which may be
10 present will depend on the kind of reactor employed
which, in turn, will depend upon the process

5 conditions required to be operated. These are
discussed further below. Where step (a) of the
15 method according to the first aspect is carried out
in a conventional stirred batch reactor, eg for
precipitating calcium carbonate, the said solids may
20 form from 0% to 20% by weight of the aqueous
suspension to be treated to give precipitation
formation therein. Desirably, such solids constitute
from 0% to 10% by weight, especially 0% to 7% by
25 weight, of the treated suspension in the use of such
15 a reactor.

In other reactors, eg to operate a continuous or
semi-continuous process, the solids content may be
30 higher, eg up to levels of 40% or even 50%.

In the composite pigment material according to
20 the second aspect of the present invention the weight
ratio of the said fine particulate material to
35 precipitated white pigment compound present may be in
the range 1:100 to 1:1, especially 1:20 to 1:2. The
white pigment compound present in the composite
25 pigment material (including any particles present in
addition to the fine particulate material) may
40 constitute at least 50% by weight, especially from
70% to 96% by weight of the material (on a dry solids
basis).

45 30 The composite pigment material according to the
second aspect of the present invention may comprise

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particles whose size will depend upon the size of the constituents used to form the particles. If desired, it is possible to treat the composite material particles produced by comminution, eg by wet stirring, milling or grinding, and optionally particle size classification as described hereinafter.

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The individual precipitate crystals which make up the matrix of the composite pigment material will generally have a size comparable with such crystals formed in the prior art (when not part of a composite structure). Generally, such crystals will be sub-micron size, eg having sizes in the range 0.1 μm to 1 μm .

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Where the fine particulate material comprises TiO_2 , the TiO_2 particles employed in the method according to the first aspect of the present invention may be of the rutile or anatase form. We prefer the rutile form. Commercially available TiO_2 pigment material may be employed. However, because the problem of retention of TiO_2 in paper making is considerably reduced by forming the composite pigment material according to the second aspect, it is possible although not essential in forming the composite material to use at least a portion of TiO_2 particles which are finer than those conventionally used, eg having a size of about 0.1 μm or even less.

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In the method according to the first aspect of the present invention, the fresh particles of the fine particulate material may be employed in an aqueous suspension to be treated to form a

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precipitate therein may be added in dry form to a
reactor vessel containing water or in predispersed
slurry form to the reactor vessel. In either case it
is preferred that the mixed suspension so formed
5 containing the fine particulate material is
mechanically agitated, eg by vigorous stirring,
preferably both before and during the precipitation
reaction, to ensure that the particles of the fine
particulate material are maintained in a dispersed
10 state in the suspension whilst the crystal
precipitation proceeds. If desired, a known
dispersing agent, eg a polyelectrolyte such as one of
the agents well known for the dispersion of
15 particulate materials in an aqueous suspension, eg
sodium polyacrylate, may also be present, preferably
in a small amount, eg less than 0.5 per cent by
weight.

30 The fine particulate material may be added with
vigorous mixing to an aqueous lime suspension and the
20 required precipitate may be produced by carbonating
the mixed suspension so formed. It is not necessary
35 to incorporate the fine particulate material, or all
of that material, prior to carbonating. Some or all
of the fine particulate material may be added after
25 some carbonation, ie to produce some of the
precipitate crystals. The fine particulate material
may be added in more than one dose. Each addition
may optionally be accompanied by an addition of lime
and followed by a carbonation step.
40 30 If the water employed to provide the aqueous
medium (eg to provide the aqueous suspension employed

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in step (a)) in the method according to the first aspect of the present invention contains soluble or insoluble species which will affect the process of precipitation of the white pigment compound it may be desirable to carry out a preliminary precipitation step in the water prior to introduction of the said fine particulate material which will form the composite pigment material together with the white pigment compound. For example, the employed water may be so-called white water from a paper making operation. The preliminary precipitation will entrain the species present in the white water in the manner described in EP 604,095. Up to 90% by weight, e.g. from 1% to 50%, or 10% to 50%, by weight of the white pigment compound to be formed, may be precipitated in the preliminary precipitation step(s) prior to addition of the fine particulate material. The resulting final product formed will consist of a mixture of particles of the white pigment compound, the fine particulate material and others containing only the precipitate and species originally present in the water used. The product may also contain aggregates of two or more of the various kinds of precipitate particles possible.

As noted above, the precipitated white pigment compound may comprise an alkaline earth metal carbonate, especially calcium carbonate, which may conveniently be produced in a well known way by addition of a carbon dioxide-containing gas to an aqueous medium containing ions of the required alkaline earth metal (as well as the fine particles

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and the fibres when required). Such production
allows the required white pigment to be produced
without substantial undesirable production of non-
crystalline by-products as in the prior art. The
aqueous medium may in this case comprise a medium
containing a hydroxide of the required alkaline earth
metal. Such a hydroxide may comprise a hydroxide of
one or more of calcium, magnesium and barium.

Where the aqueous medium comprises a hydroxide,
the hydroxide may be separately prepared and added to
the aqueous medium or alternatively may be prepared
in situ in the aqueous medium, in each case, for
example, by slaking an alkaline earth metal oxide (eg
calcium oxide or quicklime, when calcium hydroxide is
desired). Where an alkaline earth metal oxide, eg
calcium oxide is to be slaked in an aqueous medium
either separately or in situ in the reactor vessel,
the oxide may previously be screened, eg using a
125µm screen, or a 53µm screen, to separate large
particles so that these are not present in the
slaking process.

Where the aqueous medium comprises calcium
hydroxide produced by slaking in an aqueous medium,
the calcium hydroxide will itself be in the form of a
suspension in the aqueous medium, ie so called
'slaked lime'. Calcium ions will sparingly enter
solution and will be continuously consumed and
replaced as the precipitation reaction proceeds, eg
by addition of carbon dioxide. Preferably, a
suspension formed in this way contains between from
5% to 50% by weight of the hydroxide particles.

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Desirably, there is between 0.5 mole and 3.0 moles,
especially from 1.0 to 2.0 moles, of the alkaline
earth metal hydroxide in the aqueous medium. For
slaking of lime, the temperature of the aqueous
medium may be from 0°C to 80°C. The temperature will
rise during the slaking process. If the aqueous
medium is not at the appropriate temperature after
slaking, it may be heated or cooled to achieve the
desired temperature before further use.

Efficient dispersion and dissolution of the
alkaline earth metal hydroxide may also be assisted
by agitation, eg by stirring of the aqueous
suspension, to provide uniform distribution of the
particulate solid material comprising the hydroxide.
This agitation may be combined with that applied to
the particles of the fine particulate material and
the fibres.

The source of the alkaline earth metal ions, eg
calcium oxide or calcium hydroxide (where the
precipitated compound to be formed is calcium
carbonate), may be added to water employed to form
the aqueous medium before, during or after the
addition of the fine particulate material. Where a
batch reactor vessel is employed, we prefer to add
the fine particulate material to the reactor vessel
after adding a suspension of slaked lime to the
vessel. Water may be added after any of the
individual addition stages.

Where an alkaline earth metal carbonate is to be
precipitated by addition of CO₂ to an aqueous
suspension containing a source of alkaline earth

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metal ions (and in at least part of the process also
fine particulate material) the carbonation reaction
may be carried out in a conventional vessel as is
well known to those skilled in the art of

5 precipitated carbonate production. Where the aqueous
medium comprises slaked lime, the slaked lime
suspension may be prepared in the vessel in which the
carbonation is to be carried out, or in a separate
vessel prior to introduction to the carbonation

10 vessel.

The addition of a carbon dioxide-containing gas
to an aqueous medium containing slaked lime (and, in
at least part of the process, also fine particulate
material and fibres) may be continued until the pH of
25 the aqueous medium has fallen, eg to a pH less than
9.0 preferably to a pH less than 7.5, eg by
monitoring the pH until it falls and then becomes
30 stable. This indicates that all of the alkaline
earth metal ions have been consumed, eg by
20 consumption of all calcium hydroxide present.

The reactor vessel in which the precipitation
reaction is carried out to produce the composite
material according to the second aspect of the
present invention may take various forms depending on
35 the process conditions required to be operated as
described herein. Reactor vessels known in the prior
art for the production of precipitated calcium
carbonate from slaked lime and carbon dioxide gas may
40 be employed. The reaction may be carried out as a
batch, continuous or semi-continuous process as
45 appropriate.

10 In its simplest form, the reaction vessel may be
a container in which the various ingredients to be
present in an aqueous suspension during the reaction
may be added and mixed together in the vessel and CO₂
5 gas may be bubbled into the mixture.

15 The reaction may be carried out as a continuous
or semi-continuous process in a cascade of reactor
vessels. In such an arrangement an aqueous
suspension containing lime, and where required fine
20 particulate material such as TiO₂, may be delivered to
the various vessels in sequence and carbon dioxide
may be applied to each vessel whereby the required
reaction takes place progressively along the
25 sequence.

15 Another form of reactor which may be employed
for a continuous or semi-continuous reaction is one
in which the ingredients of the aqueous suspension
30 and the final reactant, eg carbon dioxide, are mixed
together via one or more static mixers of a known
kind, eg in a known in-line arrangement. Doses of
20 individual ingredients, eg lime, fine particulate
material, or carbon dioxide, as appropriate may be
delivered via two or more mixers to give a sequence
35 of ingredient additions whereby the reaction required
25 takes place progressively in stages.

40 Preferably, during the reaction, or each stage
of the reaction, especially where fine particulate
material is present, mixing is applied. Gas such as
CO₂ which is applied may be pressurised.

45 30 The aqueous medium in which the alkaline earth
metal ions are contained and reacted with

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precipitate-forming reagent, eg carbon dioxide, in
the method according to the first aspect of the
present invention may (in addition to fine
particulate material in at least part of the process)
5 also contain one or more chemicals of a kind known
for use in precipitate production, eg it may comprise
a buffer solution to give the product so-called acid
tolerance or a frothing agent to provide efficient
reaction between CO₂ bubbles and lime, or an additive,
10 eg an organic additive, eg citric acid, to facilitate
crystal nucleation and growth.

As noted earlier, the aqueous medium in which
the composite pigment material is to be produced in
the method according to the first aspect may, (in
25 addition to added fresh particles of a fine
particulate material in at least part of the process)
also contain other fine suspended solid material
30 which may be in addition to any suspension of
consumable particles employed to provide a source of
20 alkaline earth metal ions. For example, there may be
present other fresh or alternatively previously used
35 pigment particles and/or fibres. For example, fines
collected from a waste stream from a paper making
process or a waste paper treatment or de-inking
40 process as described in copending published patent
applications EP-A-604,095 and EP-A-737,774 may also
be present prior to any precipitation step involving
the fine particulate material and, as noted
hereinbefore, may be entrained by precipitation
45 30 before the fine particulate material is present or,
alternatively whilst the particulate material is

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present. Such fines may comprise used particles
10 present in the waste stream such as organic particles
such as ink, latex or polymer particles and/or
inorganic particles such as mineral filler or coating
5 particles as used in paper making or paper coating
and/or fine fibres. Alternatively, or in addition, a
15 selection of particles from a minerals refining or
separation process or residue from an incineration
process, eg incineration of paper de-inking waste,
20 may be present as described in PCT/GB96/00884. Where
such other solid materials are included in the
treated aqueous medium they may be present in an
amount of up to 50% by weight, eg 1% to 10% by
25 weight, based on the dry weight of composite material
15 product to be formed. Where such other solids are
present in the suspension to be treated, such solids
become entrained, together with the freshly added
30 fine particulate material, and bond to the
precipitate crystals formed and thereby form a multi-
20 media mixed aggregate solid system. The aggregate
product so formed is useful in the papermaking and
35 paper coating applications described below.

Where a carbon dioxide-containing gas is
employed to provide a carbonation reaction in the
40 method according to the first aspect, the carbon
dioxide-containing gas may be substantially pure
carbon dioxide eg as commercially supplied in a
compressed gas cylinder or may be present in a
45 mixture with other gases. The supplied carbon
dioxide gas may be diluted with other inert gases, eg
air, nitrogen, etc. The carbon dioxide may be

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present as a mixture of spent gases such as flue
gases, eg obtained from a lime calcination plant in
which quicklime is produced for conversion into
slaked lime (for use in the process according to the
5 first aspect). The gas may be applied under
pressure, eg in the manner described hereinbefore.

The temperature of the aqueous medium when the
precipitate-containing composite material is formed
therein, eg when a carbon dioxide-containing gas is
10 added thereto, is preferably in the range of from 1°C
to 80°C, especially 20°C to 60°C, more preferably 30°C
to 55°C. Such an aqueous medium may be derived from
used water from a paper making plant which may have
25 an appropriate elevated temperature when delivered
15 for use in the method of the present invention.

It is known, eg as described in US-A-715,832,
30 that the reaction conditions employed to produce a
precipitated calcium carbonate product can be
selected to aim for a predominant precipitate crystal
20 form, eg scalenohedral, aragonite or rhombohedral,
which will give desired properties, eg brightness,
35 from the crystals when used in paper. Such reaction
conditions may be selected and applied in operation
of the method according to the first aspect of the
40 present invention. However, since the reaction
medium in which the crystals will precipitate in the
method of the invention is not a homogeneous one, the
crystal form of calcium carbonate achieved in
45 practice in producing the composite pigment material
30 is unlikely to be near to 100% of a selected form.
It is quite usual for one crystal form even when

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predominant to be mixed with other forms. Such mixed
10 forms will however generally give suitable product
properties because the optical properties of the
product will not result from the precipitate crystals
5 alone.

The addition of a carbon dioxide-containing gas
15 to an aqueous lime-containing suspension (with or
without fine particulate material, may be continued
until the pH of the aqueous medium has fallen, eg to
20 a pH less than 9.0 preferably to a pH of 7.5 or less,
eg by monitoring the pH until it becomes stable.
This indicates that all of the alkaline earth metal
ions have been consumed, eg by consumption of all
25 calcium hydroxide present.

15 The composite pigment material according to the
second aspect of the present invention when produced
is preferably obtained in the form of an aqueous
30 suspension which preferably has a viscosity of not
more than 500mPa.s (as measured by a Brookfield
20 Viscometer using a spindle speed of 100 rpm) and is
preferably a pumpable and flowable slurry.

35 The aqueous suspension comprising the composite
pigment material formed as a product in the method
according to the first aspect of the present
40 invention may be further processed for example by
dewatering and/or by subjecting the composite-
containing suspension to comminution, eg rapid
stirring, milling or grinding by one of several known
45 procedures.

30 As described in EP-A-768,344 such a comminution
step may be carried out by attrition grinding. In

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such grinding, the grinding medium employed in the
10 comminution step may comprise one of the hard,
inorganic materials well known in the grinding of
particulate materials. For example, silica sand
5 having a median particle diameter in the range from
about 0.1mm to 4mm, eg 0.2mm to 2mm, is a preferred
15 grinding medium. The grinding medium could
alternatively be aluminium oxide, zirconium oxide,
hard steel or a mixture of any of these materials.

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10 When the product comprising the composite
pigment material is subjected to a comminution step
the pH of the aqueous suspension containing the
product being treated may rise, as described in EP
25 768,344A, eg to pH 11 or more, as free basic
15 material, eg unconverted lime (where lime is used as
the source of alkaline earth metal ions), entrapped
in the crystalline structure comprising the composite
30 material is released by the comminution. Such a pH
level may be undesirable in the applications in which
20 the material may be employed, as described
hereinafter, because it is potentially harmful to
35 machinery and to operators who have to process the
suspension.

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An additional step to reduce the pH of the
25 aqueous suspension containing the composite pigment
material may be applied after a comminution step.
The additional step may be applied until the pH falls
to a suitable level, eg pH 10 or below, eg pH 9 or
45 below, preferably pH 7.5 or below. The additional
30 step may comprise further treatment by carbonation of
the precipitate-containing suspension.

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10 Alternatively, or in addition, a material known for
use in reducing the pH of a mineral suspension may be
added. Such a material may, for example, comprise a
mild mineral acid such as phosphoric acid.

15 5 The aqueous suspension containing composite
pigment material product formed in the method
according to the first aspect of the present
invention may be treated so as to separate partially
or fully the aqueous host medium from the composite

20 10 material solids using one or more separation
processes which may be known processes. For example,
processes such as filtration, sedimentation,
centrifugation or evaporation may be used.

25 Filtration using a filter press is usually preferred.

15 15 The separated aqueous medium, eg water, may,
optionally with further purification or clarification
by one or more chemical, biochemical or mechanical
processes which may be known per se, may be recycled
30 for reuse, eg in a paper mill, eg for use in diluting

20 20 the paper making stock or for use as showers for
washing machinery. The separated solids may be

35 35 assessed for quality control by measurements taken on
samples and subsequently delivered to a storage tank
and thereafter supplied as necessary for use in a

25 40 40 user application, eg as described hereinbefore. The
solids-containing suspension may be re-diluted for
use at the user plant.

It is not necessary for an aqueous suspension
containing a composite pigment material according to

45 30 30 the second aspect of the present invention to be
dewatered prior to supply for use in a user

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application, eg for use in paper making in a paper mill. The aqueous suspension or slurry may be delivered to a storage tank or directly to the user plant without substantial dewatering.

5 Where the composite pigment material is to be used as a filler in a paper making composition, the composite material may be supplied to the papermaking mill in one of various concentrations in water. The concentration may range from dilute suspension form
10 to dry particulate solids. The composite pigment material after preparation in the method according to the first aspect of the present invention may or may not be treated as appropriate, eg by dewatering or
20 not, so that it may be delivered to the user plant,
25 eg paper making mill, in the required concentration.

The extent of dilution or concentration of the form in which the composite pigment material product is added to the user composition, eg paper making furnish composition, does not critically affect the
30 properties of the resulting product, eg paper sheet. It may, however, for economic and practical reasons be more suitable to supply the composite pigment material product in the form of a concentrated
35 pumpable aqueous slurry. Where this product is supplied for use in a process at another location it may be preferable or desirable to dry the product
40 prior to transport. Where the product is supplied to a nearby plant it is likely to be delivered in slurry form. Where this product has been concentrated or
45 30 dried prior to delivery and subsequently re-dispersed in or diluted with clean water prior to re-use, the

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concentration and dilution steps do not materially affect the usefulness of the product.

10 In any event, where the composite pigment material product is to be used as a pigment filler

5 material in paper making, this product may, as will be clearly evident to those familiar with the paper making art, be used in a well known manner. It may be blended in various proportions with conventional filler materials, eg precipitated or natural, eg

15 ground, calcium carbonate, kaolin or other clay, calcined kaolin, talc, calcium sulfate etc, the ingredients and composition as well as the host cellulosic fibres being selected according to the quality of paper required to be produced. In

20 general, these materials are likely to be in slurry form when they are mixed. The host cellulosic fibres may be any one or more of the forms of fibers

25 employed in paper making. The fibers may be fresh or previously unused fibers, and/or recycled fibers

30 obtained from a used source, eg broke.

35 The paper maker will normally select the concentration of the composite pigment material (produced in accordance with the present invention) used in aqueous suspension form and the delivery rate

40 25 of the suspension at the point of addition to the paper making composition, eg furnish. As noted above, this may require re-dilution of a suspension which has been delivered to the paper mill in concentrated form. Generally, the composite pigment

45 30 material may form up to about 40%, usually up to about 30%, by weight of the solids content of the

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paper making composition on a dry weight basis.

Where other fillers also form part of the filler content of the paper making composition a total filler composition of up to 40% by weight of the

5 solids content of the paper composition may be employed. The composite pigment material according to the second aspect may form from 1% to 100% by weight of the added filler on a dry weight basis.

Production of a paper sheet using the paper making

10 furnish is, of course, carried out in a well known manner.

Where the composite pigment material according to the second aspect of the present invention is to be employed as a pigment material in a paper coating

25 15 composition, the composition will generally comprise an aqueous suspension of pigment, including the composite pigment material according to the second aspect and optionally other known ingredients, mixed together with a hydrophilic adhesive and optionally

30 20 other known ingredients. The composite pigment material employed in the composition may be mixed with one or more conventional pigments, eg as described above. The adhesive may form from 4% to 30%, especially 4% to 15%, by weight based on the

35 25 40 total dry weight of pigment or pigments present. The adhesive may be one of the known paper coating adhesives employed in the art, eg chosen from the group consisting of starches, proteinaceous adhesives such as casein and latices of, for example, styrene

45 30 butadiene rubbers and acrylic polymers.

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The paper coating composition may also include
one or more of the various well known optional
10 additives conventionally used in paper coating
compositions, eg a thickener, eg in an amount of up
5 to 2% by weight based upon the total dry weight of
pigment or pigments present, up to 1% by weight of a
15 soluble binder, a lubricant, eg sodium stearate
forming 0.5% of the weight of pigment present, and/or
soluble binder and/or an insolubiliser forming up to
20 1% by weight of binder present.

The paper coating composition may be formed by
mixing together an aqueous dispersed suspension of
the composite pigment material optionally with one or
25 more further aqueous dispersed suspensions containing
15 other pigments, with the adhesive and any other
optional constituents, eg thickener and/or lubricant
and/or soluble binder and/or insolubiliser, in a
30 manner familiar to those skilled in the art. Use of
the coating composition formed to coat a paper or
20 other sheet material is of course carried out in a
well known manner, eg using one of the many coating
35 machines employed in the prior art.

Precipitation of calcium carbonate in a fines-containing aqueous waste suspension, eg obtained from
40 25 a paper making waste stream, is described in EP-B-
658,606. The aqueous suspension in the process
described therein may contain waste fines which
include fine fibers and fine inorganic materials
45 30 which may incidentally include a very small
concentration of TiO₂ particles or other fine
particulate materials. However, generally, since

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these fines are used materials, they may have been produced from a variety of waste streams and therefore may be of variable composition and concentration, and they are not suitable to provide

10 5 (on their own) sources of the fine particulate material of the quality required of the fresh particles of the fine particulate material as used in the present invention. Fine particulate material such as TiO₂ derived from such waste streams will

15 10 generally be agglomerated and coagulated because of the presence of a variety of polymeric chemical additives in the waste stream and will not therefore show the benefits obtained by forming the novel composite pigment material (according to the second

20 15 aspect of the present invention) from fresh particles of fine particulate material and bonded precipitated white pigment compound such as CaCO₃ as described

25 20 hereinbefore. However, as noted above, it is possible that the aqueous medium employed in the method according to the first aspect of the present invention may optionally contain such fines as an additional solids component which will then constitute part of the composite pigment material produced.

30 25 Embodiments of the present invention will now be described by way of example only with reference to the following illustrative Examples and with reference to the accompanying drawings, wherein:

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BRIEF DESCRIPTION OF THE DRAWINGS

10 Figure 1 is a graph showing, for three different samples of composite pigment material embodying the invention, scattering coefficient of paper sheets
5 incorporating each sample as filler plotted against
15 the percentage by weight of filler (pigment) in the sheets.

20 Figure 2 is a graph showing, for a sample of composite pigment embodying the invention and in
10 comparison a sample of untreated TiO₂ in admixture
with calcium carbonate, % retention of TiO₂ in a paper
sheet incorporating each sample as filler plotted
against the percentage by weight of filler (pigment)
25 in the sheets (obtained by incineration as described
15 later).

30 In the following Examples, the properties of samples of composite pigment material embodying the invention were investigated. The samples, designated
35 Samples A, B and C, were prepared as follows.
20

SAMPLE A

35 To a stirred 5 gallons reactor, 11.4 liters of water were added. The stirrer speed was 500rpm.
40 1400 grams of lime were slowly added and the
25 temperature was kept constant at a temperature of
about 38°C throughout the addition. The lime was
slaked for 1 hour and 10 minutes. After slaking the
reactor stirrer speed was increased to 700rpm and
45 6.24 grams of citric acid were added followed by the
30 addition of 266.67 grams of titanium dioxide. To
this agitated slurry, we introduced CO₂ at a rate of

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2.52l/min and compressed air at a rate of 8.0l/min.

10 This started the carbonation of the slurry. The reaction was carried to completion.

5 SAMPLE B

15 To a 5 gallon reactor stirred at 700rpm, we added 2841ml of a 17.6% by weight precipitated calcium carbonate slurry. This slurry was carbonated for a few seconds and then we added 100 grams of

10 dispersed titanium dioxide and 2758ml of a slaked lime slurry. The slaked lime slurry had a solids concentration of 12.5% by weight. The mixture was then further carbonated by adding CO₂ at a rate of 6.0 litres per minute. The carbonation was carried to

25 completion.

30 SAMPLE C

35 To a stirred (500rpm) 5 gallon reactor, we added 11.4 liters of water. Lime (1400 grams) was added

20 very slowly in order to maintain the reactor temperature at about 38°C throughout the addition of the lime. The total slaking time was 1 hour and 10 minutes. After slaking was completed, the stirrer speed was increased to 700rpm and 6.24 grams of

25 citric acid were added. Carbonation was started by bubbling CO₂ at a rate of 2.52l/min and compressed air at a rate of 2.52l/min through the stirred slurry in the reactor. Half way through carbonation, we added 266.67 grams of titanium dioxide. The reaction was

45 30 carried to completion by continuing the addition of carbon dioxide and compressed air.

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In addition, for comparison purposes, the
following Sample D was prepared using a procedure
known in the prior art.

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5 **SAMPLE D**
A pcc product was prepared in the manner of
Sample B, except that no TiO₂ was employed during the
course of the pcc production procedure.

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Subsequently, TiO₂ was admixed with the TiO₂ to give a
10 mixture of TiO₂ and pcc in a weight ratio of 10:90,
the same target weight ratio in the composite
product, Sample B.

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EXAMPLE 1

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15 Handsheets were made with different filler
levels using the standard procedure described in
TAPPI Test Method 205. The fillers used in preparing
30 the handsheets were separately Samples A, B and C.
The furnish used in making the handsheets was a 50/50
20 blend (by weight) of soft and hard wood fibers from
Weyerhaeuser, Prince Albert, Canada. The sheet
35 formation was kept constant at around 130, as
measured by a Paprican Micro-Scanner made by OpTest
Equipment Inc. The sheet grammage was kept at around
25 75gsm⁻². The optical properties of the sheet were
measured by an instrument produced and supplied under
40 the tradename Technibrite Micro TB-IC by Technidyne
Corporation. The scattering coefficients were
45 calculated using Kubelka-Munk equations as in the
30 manner described in EP-A-604,095. The results

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obtained for Samples A, B and C are plotted as curves
10 labelled respectively A, B and C in Figure 1.

It can be clearly seen from Figure 1 that the
composite pigment material made by introducing the

5 titanium dioxide during the carbonation step had
higher scattering coefficients than the others
15 although all three materials show beneficial
scattering curves.

20 **EXAMPLE 2**

The zeta potentials of composite Sample B and
separately titanium dioxide were measured at
different pH values utilizing a charge analyzer
25 manufactured by SKS associates. The results are
15 given in Table 1 as follows.

30 **TABLE 1: Zeta Potential**

	pH7.0	pH8.0	pH9.0
Sample B	24	21	24.9
TiO ₂	-80.8	-79.2	-81.7

20 Table 1 shows that in contrast to TiO₂ untreated,
the TiO₂-CaCO₃ composite of the invention, Sample A,
40 has a positive charge potential in its surface. This
quality makes it easier to the papermaker to retain
the pigment in the sheet.

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45 **EXAMPLE 3**

Handsheets were prepared using the same
procedure as in Example 1. The filler pigments used

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in this Example 3 were separately Sample B and Sample D. Furthermore, headbox pads were obtained during the experiments, so that the retention of the fillers could be measured in a known manner. The sheets were 5 incinerated at 500°C and 950°C and the weight of ash remaining was measured. This allowed us to calculate 15 the weight percent titanium dioxide in the sheets. (The loss in weight between 500°C and 950°C allows the weight of CaCO₃ present to be determined.) The 20 results are plotted in Figure 2 in which a curve labelled B represents Sample B and a curve labelled D represents Sample D.

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As can be readily seen from Figure 2, the 30 titanium dioxide retention in the composite pigment 15 embodying the invention, Sample B, is higher than in the mixture Sample D. In fact an increase of approximately 200% can be observed.

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Claims

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CLAIMS

10 1. A method of preparing and using a composite
pigment material which incorporates a fine
5 particulate material, which method comprises the
steps of: (a) treating an aqueous medium containing
15 dispersed particles of a fine particulate material by
chemically reacting therein a first reactant and a
second reactant to precipitate therein crystals of a
20 white insoluble pigment compound thereby forming in
the aqueous medium a composite pigment material
comprising a composite matrix of precipitated
crystals of the white pigment compound and particles
25 of the fine particulate material dispersed and bonded
15 within the matrix wherein the first and second
reactants are such that they react together without
30 producing a substantial amount of non-crystalline by-
product; and (b) adding the composite material to a
composition for forming or coating a fibrous sheet
20 material.

35 2. A method as claimed in claim 1 and wherein the
fine particulate material and the first and second
reactants employed to produce the precipitation
reaction are obtained from separate stocks.

40 25 3. A method as claimed in claim 1 and wherein at
least part of the fine particulate material is fresh
material which has not previously been used in an
industrial operation.

45 30 4. A method as claimed in claim 1 and which
includes the step (c) of making or coating a fibrous

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sheet material using the composition produced in step
10 (b).

5. A method as claimed in claim 4 and wherein the
sheet material comprises paper, paper board, card,
5 cardboard or the like.

15. A method as claimed in claim 1 and wherein the
white pigment compound comprises one or more alkaline
earth metal compounds.

7. A method as claimed in claim 6 and wherein the
10 white pigment compound comprises calcium carbonate.

8. A method as claimed in claim 1 and wherein the
precipitation reaction is carried out in a batch
reactor.

25. A method as claimed in claim 1 and wherein the
15 method is carried out as a continuous or semi-
continuous process.

30. A method as claimed in claim 1 and wherein the
aqueous suspension is mechanically agitated before
and during the precipitation reaction.

20. 11. A method as claimed in claim 1 and wherein at
least one preliminary precipitation reaction is
35 carried out in the aqueous medium from which the
aqueous suspension employed in step (a) is produced,
prior to the fine particulate material being present
25 therein.

40. 12. A method as claimed in claim 11 and wherein the
fine particulate material is added to the aqueous
medium in multiple doses, a precipitate reaction
stage following each such addition.

45. 30. 13. A method as claimed in claim 1 and wherein the
white pigment compound comprises calcium carbonate

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and is obtained in the composite pigment material by
including in the aqueous suspension, together with
the fine particulate material in at least a part of
the process, calcium hydroxide, and passing a carbon

5 dioxide-containing gas into the aqueous medium to
provide precipitation of the calcium carbonate by
reaction of the calcium hydroxide and carbon dioxide.

14. A method as claimed in claim 13 and wherein the
carbon dioxide-containing gas is added until the pH

10 of the aqueous suspension falls to a value of 7.5 or
less.

15. A method as claimed in claim 1 and wherein the
aqueous medium which is treated to form the white
pigment compound by the precipitation reaction

20 comprises, in addition to the fine particulate
material, any consumable solids required as reactant
to produce the precipitate, additional solid fines
derived from a waste stream, the fines optionally
being treated by a preliminary precipitation step

25 prior to treatment in step (a).

30 35. A method as claimed in claim 1 and wherein the
temperature of the aqueous suspension when the
composite pigment material is being formed by the
precipitation reaction therein in step (a) is in the

40 45. 25 range 20°C to 60°C.

50 45. 30 30. A method as claimed in claim 1 and wherein the
composite pigment material is further treated before
addition to the paper making or paper coating
composition, the further treatment comprising one or
more of dewatering, comminution, pH adjustment and
re-dilution.

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10 18. A method as claimed in claim 1 and wherein in
step (b) the composite pigment material is added to
other pigment materials during the production of the
paper making or paper coating composition.

15 5 19. A method as claimed in claim 1 and wherein the
composite pigment material is added to the paper
making or paper coating composition in an amount
which will provide from 1% to 100% by weight of the
pigment present in the paper making or paper coating
10 composition.

20 20. Composite material for use as a pigment material
in paper making or paper coating which composite
material comprises a composite matrix of precipitated
25 crystals of an insoluble white pigment compound and
15 particles of a fine particulate material, other than
the precipitated crystals, dispersed and bonded
within the matrix, the composite material being a
30 product of treating an aqueous suspension of
dispersed, fresh particles of a fine particulate
20 material by chemically precipitating the white
pigment compound in the suspension in a reaction
35 substantially free of by-products.

35 21. A composite material as claimed in claim 20 and
wherein the fine particulate material comprises TiO₂
40 25 and the white pigment compound comprises calcium
carbonate.

45 22. A composite material as claimed in claim 21 and
wherein the weight ratio of TiO₂ to calcium carbonate
in the material is in the range of from 1:100 to 1:1.

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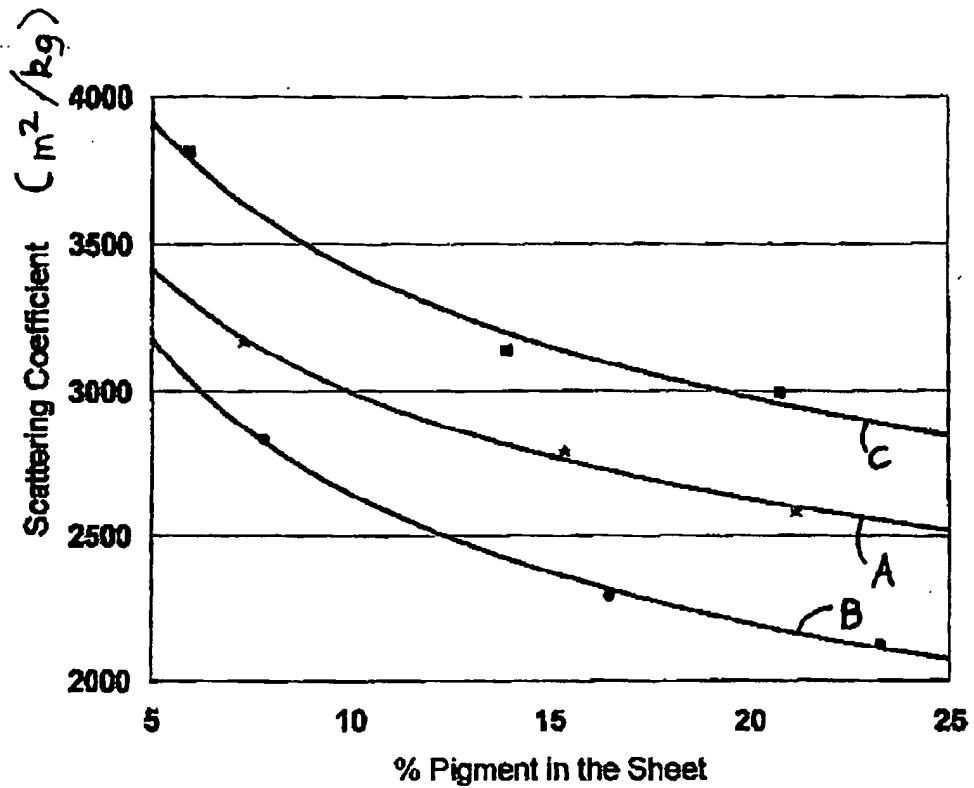


Figure 1

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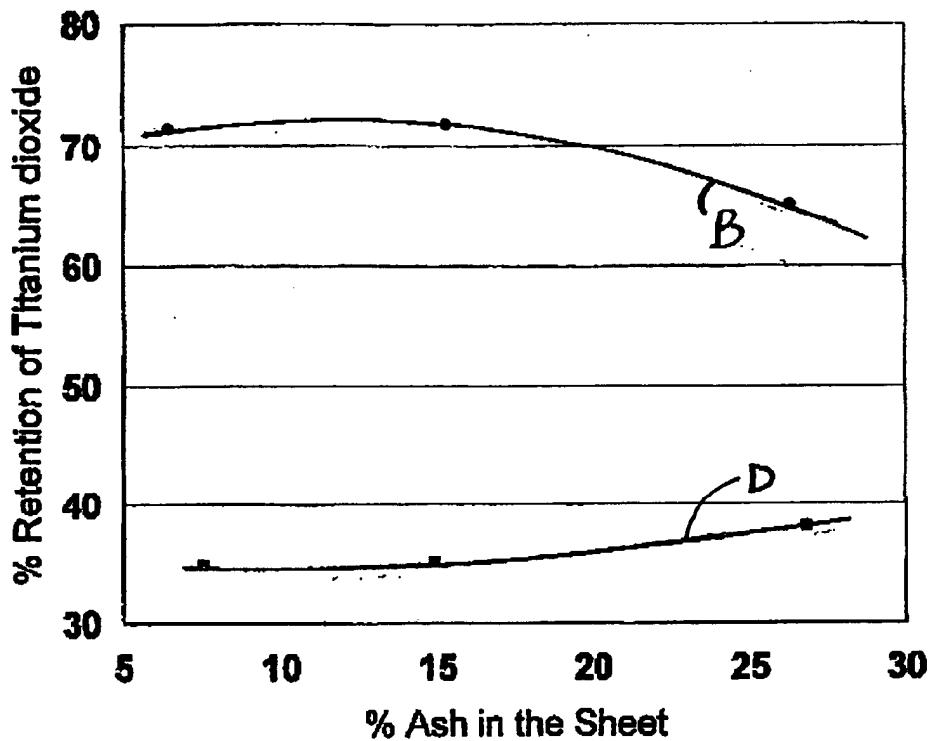


Figure 2

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 00/16610

A. CLASSIFICATION OF SUBJECT MATTER IPC 7 C09C1/00 D21H17/69 D21H19/38		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC 7 C09C D21H		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used) EPO-Internal, PAJ, WPI Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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P, A	WO 99 51691 A (ECC INT INC) 14 October 1999 (1999-10-14) claims 1-4 ---	1-10
A	EP 0 892 019 A (ECC INT LTD) 20 January 1999 (1999-01-20) cited in the application claims 1-17 ---	1-22 -/-
<input checked="" type="checkbox"/> Further documents are listed in the continuation of box C. <input checked="" type="checkbox"/> Patent family members are listed in annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed		
Date of the actual completion of the international search 26 October 2000		Date of mailing of the international search report 03/11/2000
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentdaan 2 NL - 2280 HV Rijswijk Tel: (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016		Authorized officer LIBBERECHT, E

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PCT/US 00/16610

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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